FTIR-based spectral line data of the $\nu_3$ band of NO$_2$ at 6.3 $\mu$m and multi-component impurity analysis of NO$_2$ reference gases within the scope of the EMPIR MetNO2 project

EGU GA 2020 web presentation – Session AS5.11 Atmospheric gases and particles: metrology, quality control and measurement comparability

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Overview

1. Experimental setup

2. Result of static measurements

3. Results of dynamic measurements

4. Future work
### FTIR method for impurity analysis in NO₂ standards

<table>
<thead>
<tr>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fully characterise the major impurities in the NO₂ reference gas standards (NOy compounds - especially HNO₃, NO, water vapour).</td>
</tr>
</tbody>
</table>

### NO₂ line data measurements

<table>
<thead>
<tr>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measure NO₂ line data at the wavelength range selected in A3.1.3 to support accurate NO₂ amount of substance fraction measurements and the development of spectroscopic transfer standards.</td>
</tr>
</tbody>
</table>
Experimental setup: Flow measurements

**Circulator (Julabo HE, water) for T stabilization at 296K**

**NO$_2$ reference gases in gas cabinet**

**FTIR: Bruker IFS 125HR**

**N$_2$ (from LN2 tank) gas for purging**

**Inficon P sensors**

**Gas cell: 0.8 - 8 m glass body**

**P sensor**

**MFC (coated)**

**Needle valve**

**Gas cell outlet**

**Siliconert® coated components**

**NO$_2$ reference gas**

**To pump (Vacuum out)**

**To gas cell**

**NO$_2$ leak detector**

**4 Inficon P sensors 1, 10, 100, 1000 Torr**

**Gas cell outlet**

**Gas cell**

**To gas cell**

**N$_2$ purging**

**Physikalisch-Technische Bundesanstalt - National Metrology Institute of Germany**

**Braunschweig and Berlin**
Dynamic measurement: gas flow chart

- Needle valve
- On/off valve
- Cylinder pressure
- Gas cell pressure

**Gas Cell**

- Pressure sensor 1000 torr
- Pressure sensor 1000 torr
- Pressure sensor 10 torr
- Pressure sensor 1000 torr

**Chemical pump**

- Turbo pump
- Vent Out

**NO₂ reference gas**
- MFC 200 mL/min
- N₂ gas

- Deactivated & Close
- Activated & Open

Gas cell pressure was controlled precisely using a needle valve.

- To achieve fast equilibrium state, gas cell and sampling lines were flushed using NO₂ reference gas at 500 mL/min for more than 5 min before the measurement.

- All gas lines are coated with Silconert® coating.
Static measurements: impurities

Black: FTIR spectrum of 979 µmol/mol NO\textsubscript{2} in air at 807 mbar at 296 K in a 6.4 m absorption path after a day from initial filling.

Colour: Simulation of NO\textsubscript{2} and impurities using the HITRAN database.

Impurities change dramatically with time in static measurements.

### Impurities reconstructed to t=0

<table>
<thead>
<tr>
<th>N</th>
<th>Molecule</th>
<th>Amount Fraction (µmol/mol)</th>
<th>Spectral band</th>
<th>CCQM-K74-2018* (µmol/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NO\textsubscript{2}</td>
<td>990(15); certified value from AirLiquide 979(20)</td>
<td>{ v\textsubscript{1}+v\textsubscript{3}, \ v\textsubscript{1}+2v\textsubscript{2} }, 2900 cm\textsuperscript{-1}</td>
<td>10.119(16) MY9743_7</td>
</tr>
<tr>
<td>2</td>
<td>NO</td>
<td>Not found in spectrum</td>
<td>Fundamental, 1880 cm\textsuperscript{-1}</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>N\textsubscript{2}O</td>
<td>0.790(40)</td>
<td>v\textsubscript{3}, 2224 cm\textsuperscript{-1}</td>
<td>0.027(5) MY9743_7</td>
</tr>
<tr>
<td>4</td>
<td>HNO\textsubscript{3}</td>
<td>0.430(80)</td>
<td>v\textsubscript{2}, 1709.5 cm\textsuperscript{-1}</td>
<td>0.108(36) Cyn. 614632 0.588(73) BIPM cyan.</td>
</tr>
<tr>
<td>5</td>
<td>CO\textsubscript{2}</td>
<td>0.160(20)</td>
<td>v\textsubscript{3}, 2349 cm\textsuperscript{-1}</td>
<td>0.110(92) MY9743_7</td>
</tr>
<tr>
<td>6</td>
<td>CO</td>
<td>Not found in spectrum</td>
<td>Fundamental, 2143 cm\textsuperscript{-1}</td>
<td>0.0141(19) MY9743_7</td>
</tr>
<tr>
<td>7</td>
<td>H\textsubscript{2}O</td>
<td>Not found in spectrum</td>
<td>v\textsubscript{3}, 1595 cm\textsuperscript{-1}</td>
<td>0.0105(87) MY9743_7</td>
</tr>
<tr>
<td>8</td>
<td>N\textsubscript{2}O\textsubscript{5}</td>
<td>Not found in spectrum</td>
<td>X-sections from HITRAN 1750 cm\textsuperscript{-1}</td>
<td>-</td>
</tr>
</tbody>
</table>

*Value from multiple cylinders, using GC, FTIR
Static measurements: NO₂ line intensity at 1600 cm⁻¹ band

Intensity decrease dramatically with time in an unpredictable way. Static measurement is not suitable for accurate line intensity determination.
## Dynamic measurements: spectra

**Measured FTIR spectrum**

![FTIR spectrum with highlighted regions](image)

**Selected region for line intensity determination**

![Selected region](image)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Spectrometer</strong></td>
<td>Bruker IFS125HR</td>
</tr>
<tr>
<td><strong>Resolution</strong></td>
<td>0.005 cm⁻¹</td>
</tr>
<tr>
<td><strong>SNR</strong></td>
<td>&gt;1000</td>
</tr>
<tr>
<td><strong>Source</strong></td>
<td>Globar</td>
</tr>
<tr>
<td><strong>Detector</strong></td>
<td>MCT</td>
</tr>
<tr>
<td><strong>Band pass filter</strong></td>
<td>400 – 1880 cm⁻¹</td>
</tr>
<tr>
<td><strong>Path length</strong></td>
<td>0.85 m, 1.66 m, 4.89 m</td>
</tr>
<tr>
<td><strong>Flow rate</strong></td>
<td>200 sccm</td>
</tr>
<tr>
<td><strong>Integration time</strong></td>
<td>9 hours</td>
</tr>
<tr>
<td><strong>Signal stability</strong></td>
<td>no change within 9h</td>
</tr>
<tr>
<td><strong>Pressure uncertainty</strong></td>
<td>0.3% (k=2)</td>
</tr>
<tr>
<td><strong>Path uncertainty</strong></td>
<td>0.08% to 0.25%</td>
</tr>
<tr>
<td><strong>T inhomogeneity</strong></td>
<td>0.15 K</td>
</tr>
</tbody>
</table>
Doublets with spin-splitting typically around 0.002 cm\(^{-1}\).

NO\(_2\) line intensity in HITRAN is unchanged since HITRAN96, which is based on Ref. 2.

Intensity uncertainty given by HITRAN 2-5%.

Dynamic measurements: NO$_2$ line intensity at 1600 cm$^{-1}$ band

Example Voigt$\otimes$ILS fit using PTB program

Major uncertainty components:
Amount fraction: 1%, P: 0.3%, L: 0.2%, ILS: 0.1%, Area: 0.1%
Note: HITRAN uncertainty 2-5%.
Dynamic measurements: Impurities and dimer

Two gases: Red: 98.76 ppm VSL PRM, Blue: 1007.7ppm Linde CRM

Ongoing work: quantitative results come later

“100” ppm VSL PRM:
No sign of N₂O and CO; H₂O band; HNO₃ band, trace amount of CO₂

• “1000” ppm Linde CRM
Clear N₂O band at 2225 cm⁻¹, No H₂O in sample (but inside spectrometer), clear HNO₃ band at 1710 cm⁻¹ and 1325 cm⁻¹, trace amount of CO₂

4.89 m path length
994 mbar
250 scans
Resolution: 0.2 cm⁻¹
Flow rate: 200 sccm
Future work and acknowledgement

Future work

- To improve accuracy of the NO$_2$ line intensities in the v3 band.
- To quantify impurity in the 1 ppm NPL PRM, using the 40 m siliconert coated ICL multipass cell.
- To repeat measurements to check the stability of cylinder, re-assuring line intensity accuracy.

Acknowledgement

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